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(54) Title: ENZYME DETERGENTS

(57) Abstract

Clothes are laundered by agitating in a 15 to 40 minute wash cycle by contacting with aqueous wash liquor containing surfactant and laundry enzyme and releasing a bleach into the wash liquor 20 seconds to 20 minutes after the enzyme and 10 to 20 minutes before the end of the wash cycle. Release may be by adding a coated bleach with the enzyme or by mechanical dosing.

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ENZYME DETERGENTS

The present invention re'ates to enzyme containing detergents. and especially laundry detergents. Detergents contain surfactants to remove hydrophobic soil. usually builders to increase the efficiency of the surfactant. stain removing agents and diluents. as well as various minor ingredients such as soil suspending agents. fluorescent brighteners. foam inhibitors or promoters. pH modifiers. textile conditioners. dyes. perfumes and preservatives.

Stains fall into two main categories. Many stains are decolorised by a chemical bleach which is an oxidising agent usually a peroxygen bleach such as sodium perborate. percarbonate or perphosphate or else a chlorine based oxidant such as sodium hypochlorite. chlorocyanurate or sodium chlorate.

Other stains especially proteinaceous stains are relatively resistant to oxidising bleaches but can readily be removed or reduced in intensity by laundry enzymes. Laundry enzymes are enzymes which attack various organic stains. and which are adapted to function in laundry detergent formulations (eg. at high pH such as 8 to 12 and in the presence of other laundry detergent ingredients).

Chemical bleaches. such as perborate. are effective at elevated temperatures e.g. 50 to 100°C but do not provide effective bleaching at the lower temperatures which are often used for reasons of economy in domestic washing appliances. unless an activator is present. The most commonly used bleach activator is tetraacetyl ethylenediamine (TAED). which is incorporated in almost all perborate-containing laundry detergents.

In order to maximise stain removal many detergents incorporate both an enzyme and a chemical bleach. It has been found that the optimum washing time for cost effective cleaning of laundry is 15 to 35 minutes of agitation in the wash liquor. followed by several rinses. It is known that bleach especially in the presence of activator. or at elevated temperature. can cause substantial loss of enzyme activity. To avoid this it has been proposed in the case of

severely stained articles to carry out a cold prewash with an enzyme detergent prior to the normal wash. This entails using large amounts of detergent and greatly extends the total wash time. It has also been proposed to add the bleach separately at the end of the normal wash cycle as a separate bleach stage. This also substantially extends the wash time and/or reduces the effectiveness of the bleach.

We have now discovered that even a very short delay in releasing the bleach into the wash liquor, greatly enhances the effectiveness of the enzyme whereas the effect of the bleach is not substantially reduced, provided that it is not added substantially later than 10 minutes prior to the end of the wash cycle. It is thus possible to maximise the benefit of both the enzyme and the bleach without substantially extending the total wash time or increasing the usage of detergent. We have discovered in particular that when a chemical bleach is used in enzyme detergents and the bleach and/or any bleach activator present is coated with a material which delays the release of the bleach and/or activator into the wash liquor the overall stain removal, and especially the performance in respect of enzyme sensitive stains may be dramatically improved.

According to one embodiment our invention provides a method of laundering clothes by agitating then during a wash cycle of from 15 to 40 minutes in a wash liquor comprising surfactant and enzyme characterised in that a bleach is released into said wash liquor from 20 seconds to 20 minutes after said enzyme and from 5 to 20 minutes prior to the conclusion of the wash cycle.

Laundering in said liquor is preferably continued for from 10 to 20 e.g. 12 to 18 minutes after release of the bleach, preferably at elevated temperatures, especially temperatures above 30°C e.g. 40 to 100°C and/or in the presence of a bleach activator such as tetraacetyl ethylenediamine.

According to a second embodiment, our invention provides a detergent composition of the type which comprises at least 1% by weight of a surfactant: a functional amount of an enzyme adapted to be incorporated in detergent compositions to remove or ameliorate enzyme treatable stains: 0.1 to 70% by weight of an oxidising bleach, optionally an effective amount of a bleach activator and optionally up to 80% by weight of detergent builder characterised in that said oxidising bleach is provided with a bleach-compatible, preferably inorganic coating adapted, on contact with wash water, substantially to delay, but not prevent, the release of said bleach into the wash water, and/or, where a bleach activator is present, in that said bleach activator is provided with an inorganic coating constituting at least 10% of the weight of the coated activator and adapted to delay but not prevent the release of said activator to said wash water.

The coating is preferably adapted to delay the release of the bleach by from 20 seconds up to 20 minutes. The delay may be measured by adding 0.2g of the coated bleach to 400g water containing 3mls N/10 potassium permanganate at 20°C and comparing the time taken for the pink colouration to disappear or turn brown with that observed using uncoated bleach.

As an alternative to using coated bleach, the bleach may be separately dosed to the wash liquor, e.g. using automatic dosing equipment built into the washing machine, and timed to release the bleach into the wash liquor within 20 minutes of the commencement of the wash stage. The preferred delay is from 1 to 7 minutes e.g. from 1.5 to 6 minutes.

Thus according to a further embodiment our invention provides equipment for laundering comprising a washing chamber adapted to agitate laundry with wash liquor during a 15 to 40 minute wash cycle, means for inserting and withdrawing laundry into and from said washing chamber, means for supplying water to said washing chamber at the commencement of said wash cycle, means for draining wash liquor from said wash chamber at the conclusion of said wash cycle and automatic dosing means adapted to dose detergent to said chamber before and/or during said wash cycle characterised in that said dosing means comprises a first doser adapted to dose enzyme-containing detergent to said chamber at the latest 15 minutes prior to

the conclusion of said wash cycle and a second doser adapted to dose bleach to said washing chamber from 20 seconds to 20 minutes after the dosing of said enzyme-containing surfactant and from 5 to 20 minute prior to the conclusion of said wash cycle.

The enzyme is typically a protease and especially one adapted to act at alkaline pH, eg 7.5 to 10. Other laundry enzymes include amylase, lipases, cellulases and decarboxylases. The enzyme is present in an amount adapted to substantially reduce or remove enzyme treatable stains. The enzymes may be present according to our invention in hitherto conventional amounts to provide a composition with greatly (eg, up to 100%) enhanced bleaching effects on enzyme treatable stains, without substantial loss of efficiency against oxidisable stains. Alternatively, the amount of enzyme may be reduced by up to 50% and sometimes as much as 90% compared with currently preferred levels by use of bleaching systems according to the invention, without substantial loss of performance against either enzyme treatable or oxidisable stains. Although normally present in very small proportions by weight, enzymes can account for up to a third of the cost of a laundry detergent. The invention can therefore provide substantial economic savings.

Typically we prefer detergent compositions with a total protease activity of from 0.005 to 2 Kilo Novo Protease Units per gram eg, 0.01 to 1 especially 0.1 to 0.5 KNPU per gram. We especially prefer detergents which have an amylase activity from 0.05 to 20 Kilo Novo Units per gram, eg, 0.1 to 10 especially 0.5 to 5.

The bleach is typically a perborate, percarbonate or perphosphate, such as a peroxyhydrate of tetra sodium pyrophosphate, but may alternatively or additionally comprise a chlorinating bleach.

The bleach is normally present in proportions of from 0.5 to 30% based on the weight of the composition. The uncoated particles preferably have a size between 200μ and 2mm more preferably 500μ to 1.5mm and an average size of 0.5 to 1.5mm.

In the following discussion references to the coating of bleach may additionally or alternatively apply to the coating of bleach activator mutatis mutandis.

The bleach is preferably coated with a relatively thick layer (eg. more than 10% preferably more than 15% especially more than 20% most preferably more than 30% by weight, based on the total weight of the coated bleach) of a bleach-compatible inorganic solid. The inorganic solid is preferably an ingredient normally included in laundry detergents, eg, as a builder or filler. Builders commonly used include sodium tripolyphosphate, zeolite and sodium carbonate. Fillers typically comprise sodium sulphate. It is preferred that the coating consists, at least predominantly, of slowly water soluble inorganic salts such as sodium tripoly phosphate or sodium sulphate, which will substantially delay the dissolution of the coated bleach. The coating may comprise any bleach activator present. By using normal ingredients of the detergent as, or as part of, the coating it is possible to use very thick coatings, eg, up to 400% by weight of the bleach or even higher without excessively diluting the amount of bleach in the formulation. However, we generally prefer thicknesses of from 25 to 100% of the total weight of the coated bleach.

The preferred thickness of the coating is dependent on its solubility, and in particular its rate of solubility, and its permeability, which may depend on its integrity as well as its composition. The method of application can therefore can therefore be of significance. We prefer that the coating be selected so as to permit substantially complete dissolution of the bleach during a normal wash cycle, but little or, preferably, no release of available oxygen into the wash liquor during the early stages of the cycle.

Typically the bleach is in the form of granules which release less than 10% by weight of their available oxygen, more preferably less than 5%, eg, less than 1%, in the first ten seconds after contact of 1gm coated bleach per litre with water at 40°C and more than 90% preferably 100% after 8 minutes, more preferably after 7 minutes especially after 5 minutes.

It has been found that sodium sulphate is effective at proportions of 20 to 70% by weight on particles of 1mm average size. Sodium tripolyphosphate may require or tolerate higher proportions, eg. over 100% by weight of the coated granule.

The coating is preferably substantially inorganic, since many of the organic coatings which have been used in the past to provide controlled release of various kinds of active ingredients are chemically incompatible with strong oxidising agents and may even cause fire or explosion hazards.

However, we do not exclude the use of peroxide compatible organic material, or of the use of organic coatings in conjunction with inorganic coatings, eg, as an outer layer separated from the bleach by an inert inorganic layer. Suitable organic materials for use in this way may include low melting waxes, oils such as silicone and mineral oils, surfactants, film forming polymers such as polyvinyl alcohol, polyvinyl pyrrolidone and polycarboxylates including polymaleates and polyacrylates, proteins such gelatin and casein, gums such as gum tragacanth, guar gum, gum benzoin or gum acacia, cellulose derivatives such as methyl cellulose or carboxy methyl cellulose, carbohydrates such as starch, dextrin or maltose and phospholipids such as lecithin.

The organic coating may be one that melts or dissolves in the wash water at normal wash temperature or may be physically disrupted by the washing action.

The surfactant is preferably any of the conventional laundry surfactants.

The detergent formulations of the invention typically contain from 1% to 90% by weight of surfactant, more usually 2% to 70% eg. 3% to 60% especially 4% to 50%, preferably 5% to 40%, more preferably 6% to 30%, most preferably 7% to 20%.

For example the surfactant may be, or may comprise, one or more anionic surfactants such as an alkyl benzene sulphonate, alkyl sulphate, alkyl ether sulphate, paraffin sulphonate, olefin sulphonate, alkyl ether sulphonate, alkylphenyl sulphate, alkyl phenyl ether sulphate, alkyl sulphosuccinate, alkyl sulphosuccinamate, alkyl isethionate, alkyl sarcosinate, soap, alkyl ether carboxylate, alkyl ether polycarboxylate, alkyl tauride, alkyl phosphate, alkyl ether phosphate or alkyl or thiol capped polyelectrolytes such as an alkylthiol capped polymaleic acid.

All references to "alkyl" groups in this context refer to C_8 to $_{22}$ straight or branched chain alkyl or alkenyl groups. "Ether" refers to glyceryl, mono- or poly- ethyleneoxy, mono or poly propyleneoxy, or mixed ethylenoxy/propyleneoxy, glyceryl/ethyleneoxy, glyceryl/propyleneoxy or glyceryl/ethyleneoxy/propyleneoxy.

The cation of the aforesaid anionic surfactants is usually sodium but may also be potassium or mono-, di-or tri-alkylolamine. Less commonly the cation may be lithium, ammonium, calcium, magnesium, zinc or a mono- di- or tri- alkyl amine such as isopropylamine or trimethylamine.

The surfactant may also be, or may comprise, one or more non-ionic surfactants such as the polyalkoxylated derivatives of alcohols, carboxylic acids, alkyl phenols, alkylamines, alkanolamides, or glyceryl or sorbitan esters, wherein each compound has an "alkyl" group as hereinbefore defined, and the polyalkylene oxy group comprises from 1 to 50 ethyleneoxy and/or propyleneoxy groups.

Alternatively the non-ionic surfactant may be an alkanolamide, eg. a mono- or di-alkanolamide, a lactobionamide, an alkylpolyglycoside or an amine oxide, or an alkyl or thiol capped polyvinyl alcohol or polyvinylpyrrolidone, or a sugar ester.

The surfactant may be, or may comprise, one or more amphoteric surfactants such as a betaine or sulphobetain, and/or one or more cationic surfactants such as an alkyl trimethyl ammonium, alkyl pyridinium, alkyl dimethylbenzylammonium, alkyl isoquinolinium, alkyl imidazoline or alkylamido amine. The counter ion of the cationic surfactant may typically be chloride, methosulphate, formate, acetate, citrate, lactate, tartrate or bromide.

Mixtures of anionic surfactants and non-ionic surfactants are particularly favoured: mixtures of anionic and/or non-ionic surfactants with amphoteric surfactants are also favoured, as are mixtures of cationic with amphoteric surfactants, with or without non-ionics. Mixtures of anionic with cationic surfactants are not normally favoured.

The detergent composition typically contains a total of up to 90% by weight of builder, in addition to the bleach, which may also function as a builder in the formulation, and including any builder present in the bleach coating.

Most commonly the detergent formulation contains from 1% to 80% builder, eg. 5% to 75%, more usually 10% to 70% preferably 15% to 60%, more preferably 20% to 50%, most preferably 25% to 40% by weight based on the total weight of the composition.

The builder may be any substance that assists the action of the surfactant by ameliorating the effects of calcium in the wash liquor and/or maintaining alkalinity in the wash.

The builder may for example be, or may comprise, an alkali metal orthophosphate or condensed phosphate, especially sodium tripolyphosphate, tetrasodium or tetrapotassium pyrophosphate or sodium tetraphosphate, or a phosphonate, zeolite, citrate, ethylenediamine tetracetate, nitrilotriacetate, silicate or carbonate.

The detergent compositions of this invention usually contain a filler or diluent which is typically sodium sulphate, in proportions up to 80%, more usually 10 to 60% by weight. Liquid detergents containing water as diluent are also provided.

The detergent formulations of this invention may optionally contain any of the detergent ancillary ingredients. For convenience the term "detergent ancillary ingredients" will be used herein to include all those ingredients other than surfactant, oxidising bleach, enzyme, builder and any filler or diluent, which have been or may be used to enhance the performance, appearance, pourability, stability, fragrance or ease of use of detergent compositions.

The term includes, for instance, soil suspending agents such as sodium carboxymethyl cellulose, optical brighteners, photoactive bleaches, chelating agents, sequestrates, buffers, foaming agents, foam stabilisers, antifoams, preservatives, biocides, bleach activators, enzyme stabilisers, hydrotropes, polymers, dyes, vegetable oils, mineral oils, pigments, fragrances, abrasives, perfume enhancers and fabric conditioners, including cationic fabric conditioners and inorganic fabric conditioners such as bentonite.

Compositions of the invention preferably contain soil suspending agents such as sodium carboxymethyl cellulose typically in proportions of from 0.01% to 3% by weight based on the weight of the composition, especially 0.1% to 2% eg. 0.5% to 1.5%.

The compositions typically contain fragrances, dyes, pigments and/or preservatives in a total proportion of from 0.1% to 5% by weight, eg. 0.5% to 3% by weight based on the total weight of the composition.

The compositions of the invention may also comprise conventional amounts of bleach activators such a tetracetylethylenediamine, foam control agents such as silicone antifoams and/or mineral oils where the compositions are intended for use in front loading washing

machines. or foam boosters where the products are intended for hand washing or use in top loading washing machines.

Detergent ancillary ingredients. are normally present in a total concentration below 10% by weight based on the total composition.

We prefer the particles of bleach and/or activator to be coated using powder. slurry or solution coating techniques. A spray evaporator/agglomerator can be used for this purpose. Powder coating may be accomplished by establishing differential air flow rates within a fluidised bed e.g. using baffles. It is possible to spray the coating material onto the particles in an agglomeration zone in the spray agglomerator. Alternatively the bleach may be coated by spraying a slurry or solution onto a fluidised bed of the bleach.

Alternatively products of the invention may be made by pelletising. marumerising or tabletting and references to particles and granules are to be construed broadly covering pellets. marumes and tablets without any limitations of shape or size other than those imposed by practical and commercial considerations.

The invention will be illustrated by the following examples :

EXAMPLE 1

500g of a commercial sodium percarbonate (granule size 500 μm to 1000 μm. available oxygen content = 13.8%) was charged to a Niro-Aeromatic Strea-1 Fluid-bed spray-coater/ agglomerator. The percarbonate granules were spray coated with 30 wt% slurry of sodium tripolyphosphate (STPP) in water to give a final STPP.6H2O coating weight of 100% based on the weight of the percarbonate granules.

The spray-coating conditions are listed below:

Nozzle size = 1.2mm

Spray-rate = 10g/min

Atomising air pressure = 2.5 bar

Fluidising air temperature = 80°C

1038g of coated product was produced having an available oxygen concentration of 6.7wt%.

The wash performances of the commercial uncoated percarbonate and the coated percarbonate were then compared to an uncoated sodium perborate standard

	TEST FORMULATIONS		
	A	B	C
% Sodium Perborate Monohydrate	16	-	-
% Sodium Percarbonate	-	17	-
% Coated Sodium Percarbonate	-	-	36
% Sodium Tripolyphosphate	30	30	16
% Sodium Carbonate	10	-	-

	TEST FORMULATIONS		
	A	B	C
% Sodium Sulphate	15	24	19
% Others	29	29	29

The "Others" were the same in all cases and comprised surfactants, TAED, other normal detergent ancillary ingredients and a Sarmase/Esperase/Termarryl Enzyme system at 1.7% of

the total test formulation weight. All Formulations have the same bleach available oxygen content and the same total builder content.

The test formulations were freshly prepared and used in a Miele washing machine on the "cotton short wash" cycle with "water plus" operating. The test formulation dose used was 50g per wash. The water hardness was 200 ppm calcium carbonate. Washes were carried out at 40°C and 60°C.

The percentage soil. bleachable stain and enzyme sensitive stain removals of standard cloths were determined by reflectance measurements.

	TEST FORMULATIONS		
	A	B	C
% Soil Removal at 40°C	67.3	67.2	68.3
60°C	78.5	78.4	78.7
% Bleachable Stain Removal at 40°C	56.5	59.3	55.7
60°C	70.7	72.5	71.5
% Enzyme Sensitive Stain Removal at 40°C	32.4	32.0	40.5
60°C	45.3	46.5	62.1

Soil and Bleachable Stain Removals are equivalent in all cases.

The removal of Enzymatic Sensitive Stains when using the coated percarbonate (Test Formulation C) is substantially increased.

EXAMPLE 2

750g of sodium pyrophosphate tris-peroxy-hydrate (perphosphate) granules (size range 500µm to 1000µm. available oxygen concentrations = 12.8 wt%) was charged to a Niro-Aeromatic Strea-1 Fluid-bed spray coater/agglomerator.

The perphosphate granules were spray-coated with a 30 wt% sodium sulphate solution to give a final sodium sulphate coating weight of 50% based on the weight of the perphosphate granules. The spray-coating conditions are listed below:

Nozzle size = 0.8mm

Spray-rate = 10 g/min

Atomising air pressure = 1.2 bar

Fluidising air temperature = 80°C

1128g of coated product was produced having an available oxygen concentration of 8.2wt%.

The wash performance of the coated perphosphate was compared to an uncoated perborate standard. The wash test conditions were the same as used in Example 1.

	TEST FORMULATIONS	
	A	**B**
% Sodium Perborate Monohydrate	16	-
% Coated Perphosphate	-	29.3
% Sodium Tripolyphosphate	30	16

% Sodium Sulphate	13	13.7
% Others	41	41
% Soil Removal at 40°C	66.3	65.8
60°C	76.9	75.7
% Bleachable Stain Removal at 40°C	58.7	58.8
60°C	72.9	71.7
% Enzyme Sensitive Stain Removal at 40°C	28.5	40.1
60°C	35.6	55.1

Soil and Bleachable Stain Removals are equivalent in both cases.

Enzyme Sensitive Stain Removal is much enhanced using the coated perphosphate.

Further Enzyme Sensitive Stain Removal tests were carried out under the same conditions. Formulation A with double the enzyme content gave Enzyme Sensitive Stain Removals at 40 and 60°C of 39.7% and 53.7%, respectively. These are equivalent to the results from Test Formulation B. Formulation B with half the original enzyme content gave Enzyme Sensitive Stain Removals at 40 and 60°C of 35.2 and 47.6% respectively. These are still significantly better than Test Formulation A.

EXAMPLE 3

Laundry evaluations of the enzyme powder test formulation A of Example 1, in which the sodium perborate monohydrate was replaced with an equal weight of uncoated sodium percarbonate, were carried out at 40°C and 60°C and compared with runs in which the bleach component of the formulation was added separately from the other components, at various intervals up to 10 minutes after the commencement of the wash cycle.

The results are set out ir the following Tables.

40°C

DELAY (mins)	0	1	5	7	10
%SOIL REMOVAL	71.81	73.16	73.45	72.38	71.82
%BLEACHABLE STAIN REMOVAL	61.57	61.00	60.68	60.01	54.27
%ENZYME SENSITIVE STAIN REMOVAL	41.97	57.27	64.99	67.14	65.23

60°C

DELAY (mins)	0	1	5	7	10
%SOIL REMOVAL	79.75	81.11	81.08	79.63	79.92
%BLEACHABLE STAIN REMOVAL	75.48	75.69	75.03	74.18	71.60
%ENZYME SENSITIVE STAIN REMOVAL	45.30	62.40	65.56	68.08	69.31

CLAIMS

1. A method of laur dering which comprises agitating laundry during a wash cycle of from 15 to 40 minutes with an aqueous wash liquor containing surfactant and stain reducing enzyme characterised in that an oxidising bleach is released into the wash liquor from 10 seconds to 20 minutes after said enzyme, and from 5 to 20 minutes prior to the conclusion of the wash cycle.

2. A method according to claim 1 characterised in that the wash cycle is continued for from 10 to 20 minutes after the release of the bleach.

3. A method according to claim 2 wherein said continued wash cycle is effected at a temperature of 30 to 100°C and/or in the presence of a bleach activator.

4. A method according to any foregoing claim comprising : (i) contacting laundry with an aqueous wash liquor, containing surfactant and stain-reducing enzyme; (ii) agitating said laundry in said wash liquor for from 0.5 to 20 minutes, while heating said wash liquor to a temperature above 30°C; releasing an oxidising bleach into said wash liquor at the end of step (ii); agitating said laundry in said wash liquor for a further 5 to 20 minutes; and (iv) draining and rinsing said laundry.

5. A method according to any foregoing claim wherein the release of said bleach is effected by automatic dosing means.

6. A method according to any of claims 1 to 4 wherein said bleach is provided with a coating adapted to delay the release of the bleach into the wash liquor and the coated bleach is added to the wash liquor with the enzyme.

7. A detergent composition of the type which comprises at least 1% by weight of a surfactant: a functional amount of an enzyme adapted to be incorporated in detergent compositions to remove or ameliorate enzyme treatable stains: 0.1 to 70% by weight of an oxidising bleach, optionally an effective amount of a bleach activator and optionally up to 80% by weight of detergent builder characterised in that said oxidising bleach is provided with a bleach-compatible, preferably inorganic coating adapted, on contact with wash water, substantially to delay, but not prevent, the release of said bleach into the wash water, and/or, where a bleach activator is present, in that said bleach activator is provided with an inorganic coating constituting at least 10% of the weight of the coated activator and adapted to delay but not prevent the release of said activator to said wash water.

8. A detergent composition according to claim 7 wherein the coating is adapted to delay the release of the bleach by from 20 seconds to 20 minutes.

9. A composition according to either of claims 7 and 8 wherein the bleach is perborate, percarbonate or perphosphate.

10. A composition according to any of claims 7 to 9 wherein said bleach and/or said bleach activator has a particle size between 200μ and 2mm and is coated with from 25 to 100% by weight of bleach-compatible inorganic solid based on the total weight of the coated particles.

11. A composition according to any of claims 7 to 10 wherein said coating is sodium sulphate and or sodium tripolyphosphate.

12. A laundry detergent composition according to any of claims 7 to 11 comprising 2 to 7% by weight surfactant, 5 to 75% by weight builder, 10 to 60% by weight filler or

diluent. 0.5 to 30% by weight active bleach an effective amount of stain-reducing enzyme and 0 to 10% of ancillary ingredients including any bleach activator.

13. A laundry detergent according to any of claims 7 to 12 substantially as described herein with reference to any one of the examples.

14. A coated granule for use in a laundry composition according to claim 7 having a size from 200μ to 2mm and consisting essentially of sodium perborate, percarbonate and/or perphosphate coated with from 25 to 100% by weight of said granule of inorganic bleach compatible solid.

15. Equipment for laundering according to claim 5 comprising a washing chamber adapted to agitate laundry with wash liquor during a 15 to 40 minute wash cycle, means for inserting and withdrawing laundry into and from said washing chamber, means for supplying water to said washing chamber at the commencement of said wash cycle, means for draining wash liquor from said wash chamber at the conclusion of said wash cycle and automatic dosing means adapted to dose detergent to said chamber before and/or during said wash cycle characterised in that said dosing means comprises a first doser adapted to dose enzyme-containing detergent to said chamber at the latest 15 minutes prior to the conclusion of said wash cycle and a second doser adapted to dose bleach to said washing chamber from 20 seconds to 20 minutes after the dosing of said enzyme-containing surfactant and from 5 to 20 minute prior to the conclusion of said wash cycle.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D D06L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,89 08695 (NOVO INDUSTRI) 21 September 1989 see claims 1,4,5	7,9
X	EP,A,0 206 959 (ATOCHEM) 30 December 1986 see page 3, line 15 - line 17; claims 1,4,10	1-4
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Inter. ional Application No
PCT/EP 96/00668

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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P,X	WO,A,95 28467 (PROCTER & GAMBLE) 26 October 1995 see page 5, paragraph 4 see page 6, paragraph 3 see page 20, paragraph 6-7 see page 26, paragraph 4-5 see page 35, last paragraph - page 36, paragraph 1	7,9, 11-14
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P,X	WO,A,95 28463 (PROCTER & GAMBLE) 26 October 1995 see page 7, line 15 - line 18; claim 1	7,9

P,X	WO,A,95 17495 (PROCTER & GAMBLE) 29 June 1995 see page 2, last paragraph - page 3, paragraph 2 see page 20, paragraph 2; claims 1,4,7	7,9
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